Quarterly Progress Report

For the project entitled:

Inhibitor Longevity and Deicer Performance

Reporting Period: July 1, 2008 – October 15, 2008

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Task 0: Project Management

Weekly meetings were held between team members and the Principal Investigators. As a result of these meetings, experimental design, planning issues, laboratory methods, and items for the field investigation were discussed so that testing was conducted in a timely manner.

The Steering Committee made a site visit to the Western Transportation Institute in Bozeman, MT, to tour the laboratory facilities and visited *Transcend* in Lewistown, MT, to see the field site. The meeting notes are attached as Appendix A.

Personnel updates include the increased role of Mr. Doug Cross in Task 3 (Field Investigation) and Mrs. Marijean Peterson in Task 2 (Laboratory Investigation). An undergraduate research student will be funded through the WTI-URE fellowship program to participate in this research project.

Task 1: Experimental Design and Planning (50%)

Planning for Task 3.1

The final product to be tested in the field will be determined by the Steering Committee and TAC to fill in for the category 4 product that was originally selected from the PNS Qualified Product List. Once decided upon the product will be obtained and delivered to the site, and a confidentiality agreement will be established between MSU and the company that produces the product.

Modifications will be made to the field site to winterize the equipment, to prevent snow drifts from limiting site access, and to cover the open side of the buildings in order to prevent precipitation from reaching the solid material piles. In addition, a small-scale collection pad will be built on site to better assess the quantity of precipitation and evaporation that the outsides piles experience. This will allow us to better assess what percent of liquid is cisterns are storing relative to total precipitation.

Planning for Task 3.2

Liquid and solid application equipment that would meet the needs of the project has been identified and will be purchased. We will test both stream and spray liquid applicator nozzles in the laboratory to determine percent recovery. These data will then be reported back to the Steering Committee so that a decision can be made on the type of nozzle to be used for the field investigation. The liquid and solid applicators will be mounted on a tow trailer, both of which are designed for agricultural applications. The equipment allows us to apply small quantities (to be specified by the Steering Committee and TAC) of deicer products for the field operational tests, with precision in application rate. Testing of the liquid and solid application equipment will begin in the next quarter (Fall/Winter of 2008) to ensure we can reproduce the application rate and recover the material applied.

Standard operating procedures (SOPs) are being developed for the simulation of each storm event identified (creating “artificial” storms), the application of deicers (liquid and solid) on pavement, and the collection of deicer samples from the field pavement. The SOPs are designed to minimize the uncertainties and risks in the field investigation.

Transcend

- We are working closely with the *Transcend* team at WTI (including Eli Cuelho, Michelle Akin, and Jason Harwood) to ensure the success of this project. The current date for the power, water, and snow-making equipment to be in place and operational at *Transcend* is December 19, 2008.
- The building at *Transcend* will be in place by the end of January 2009.
- The facility contractors are mobilized on site and work is currently underway.
- A well has been drilled and reached water at 600ft with sufficient flow to run the snow-making equipment.
- Pavement temperature sensors will be in place by the end of November 2008.

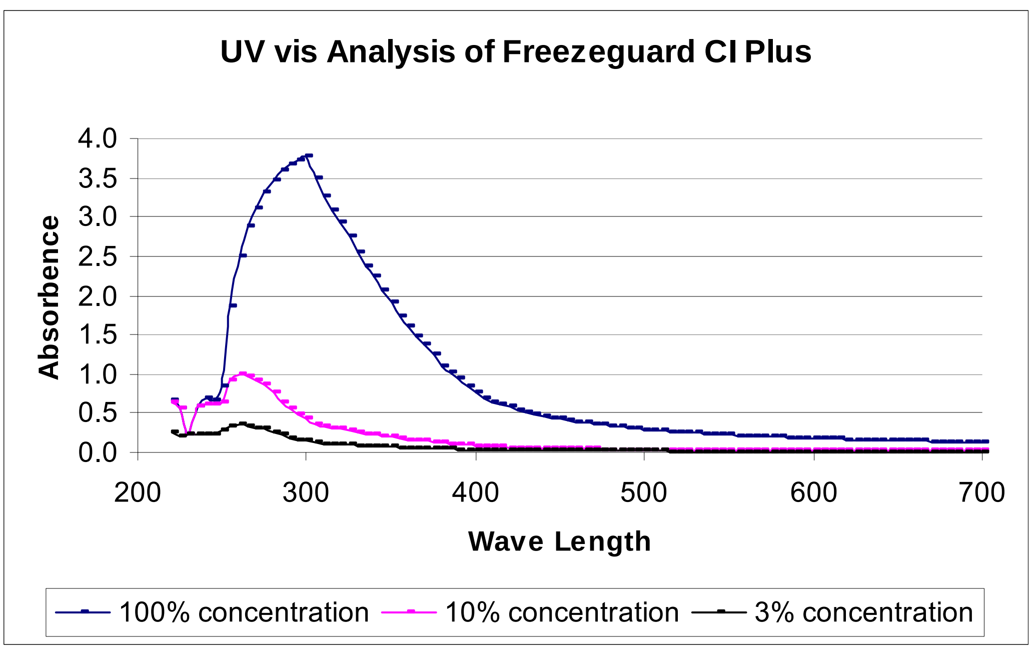
Task 2: Laboratory Investigation (70%)

Task 2.1: Method to Rapidly Quantify Inhibitor Concentrations (75%)

UV-Vis

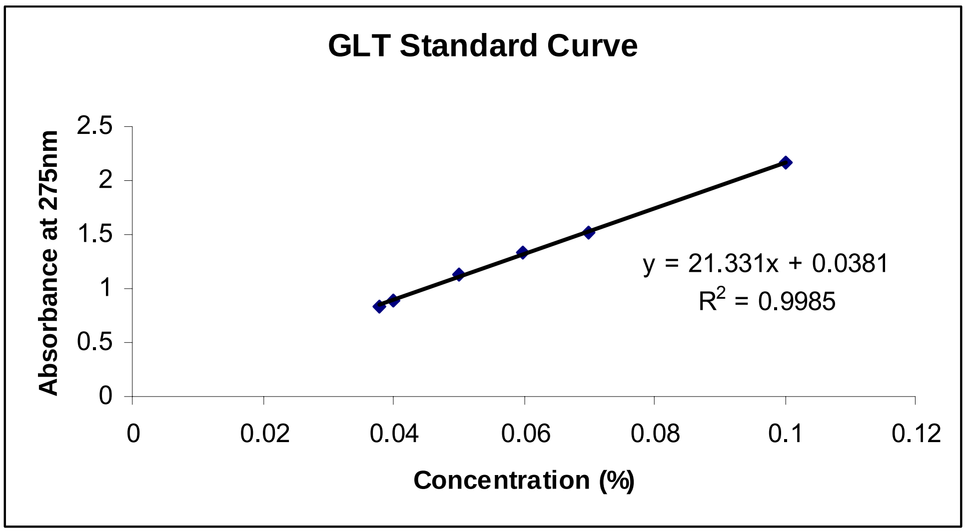
The ultraviolet-visible spectroscopy or spectrophotometry (UV-vis) is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The research team is identifying the characteristic UV-absorption peak for each of the selected corrosion inhibitors. Figure 2.1 shows the characteristic UV-absorption peak for Freezeguard CI Plus at varying concentrations. Once the characteristic UV-absorption peak is determined (e.g., near 260 nm) for each corrosion inhibitor a standard curve can then be made which correlates the inhibitor concentration with the UV signal intensity.

Figure 2.1 UV-vis analysis of varying concentrations of Freezeguard CI Plus deicer.



For each corrosion inhibitor of interest, the research team is preparing standard solutions with known inhibitor concentrations (using de-ionized water as the solvent), and analyzing them with UV-vis spectrophotometer. The presence of the inhibitor will give a response (e.g. optical density) proportional to the concentration. As such, a standard calibration curve can be established for each inhibitor. Figure 2.2 shows the standard calibration curve for GLT corrosion inhibitor (R^2=0.99). For any field samples with unknown inhibitor concentration, the measured UV-vis absorbance of the sample can be compared against the calibration curve to derive the inhibitor concentration.

Figure 2.2 UV-vis standard curve showing the analysis of varying concentrations of GLT corrosion inhibitor.



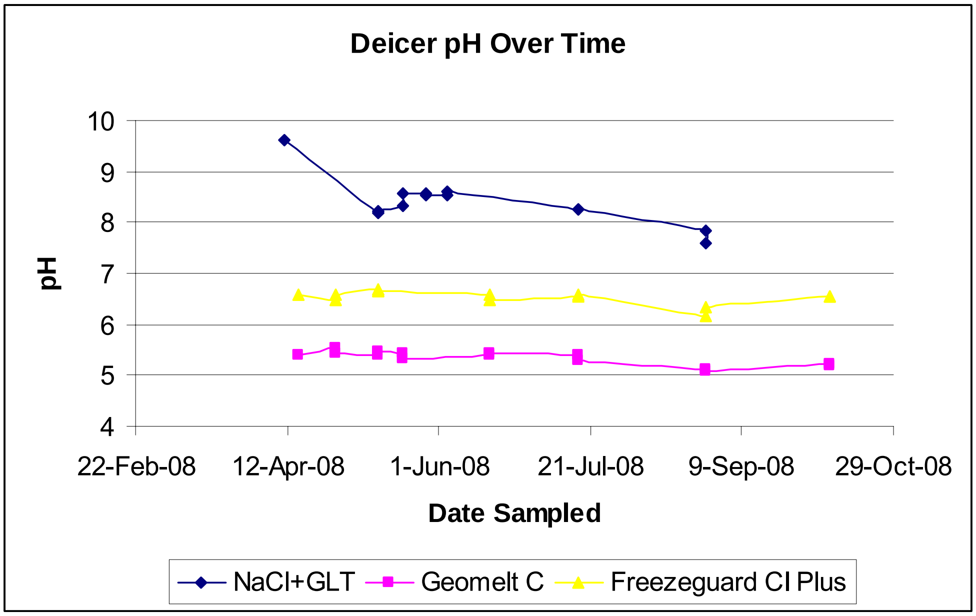
Chloride Concentration of Deicers

The chloride concentration of all samples was determined with a chloride ion selective probe (WQ-CL Smart USB Chloride Sensor, Nexsens Technology). See Task 3.1 for chloride concentration data.

pH of Deicers

The pH of the deicers was measured using an AB15 pH meter (Accumet, Fisher Scientific). Figure 2.3 shows the change in pH of the three liquid deicers over time.

Figure 2.3 Measured pH of deicer solutions over time.



Task 2.2.: Method to Rapidly Quantify Corrosivity of Deicers (95%)

PNS/NACE Corrosion Test

The PNS/NACE test is based on a gravimetric method that entails cyclic immersion of multiple parallel coupons for 72 hours on a custom design machine. The weight loss result in MPY (milli-inch per year) is translated into a percentage, or percent corrosion rate (PCR), in terms of the solution corrosivity relative to a eutectic salt brine. Testing with the Corrosion Testing Machine (Ad-Tek, Inc) as specified in the PNS/NACE modified gravimetric test has begun. Figures 2.4-2.6 show the measured weight loss results in MPY for samples collected from the field (which can be translated to corrosivity data in PCR later).

The preliminary data reveal that: 1) All but one of the sampled deicers tested passed the PNS/NACE requirement: being at least 70% less corrosive than the reagent-grade eutectic salt brine; 2) The PNS/NACE test has been generating reproducible data for each deicer tested at a certain “shelf life” (based on the small standard deviation bars in the plots); 3) Generally the corrosivity of the deicers tested has not showed any increase over time and the fluctuations in the deicer corrosivity over time may have been derived from the deicer sampling process.

Figure 2.4 PNS/NACE cyclic emersion corrosion test results for NaCl+5% GLT, where ***m*** represents samples mixed in the field and ***nm*** represents samples not mixed.

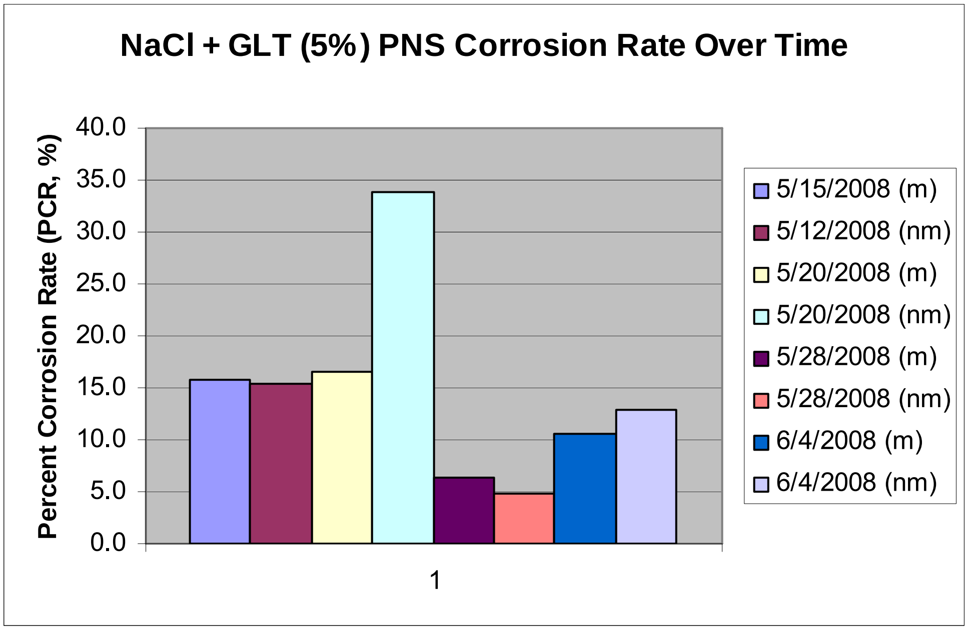


Figure 2.5 PNS/NACE cyclic emersion corrosion test results for Freezeguard CI Plus, where ***m*** represents samples mixed in the field and ***nm*** represents samples not mixed.

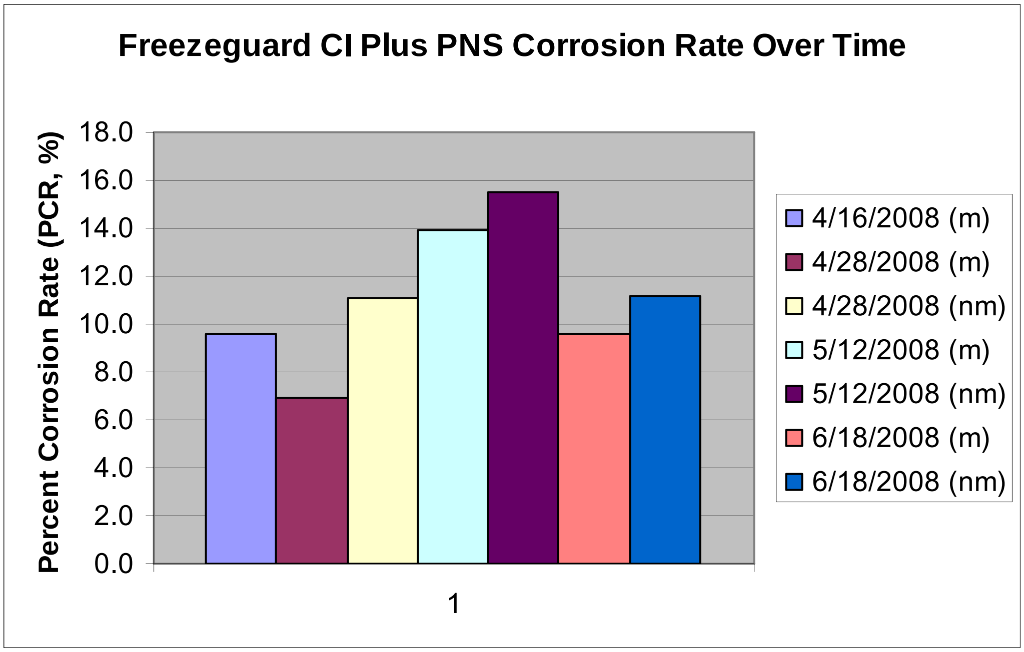
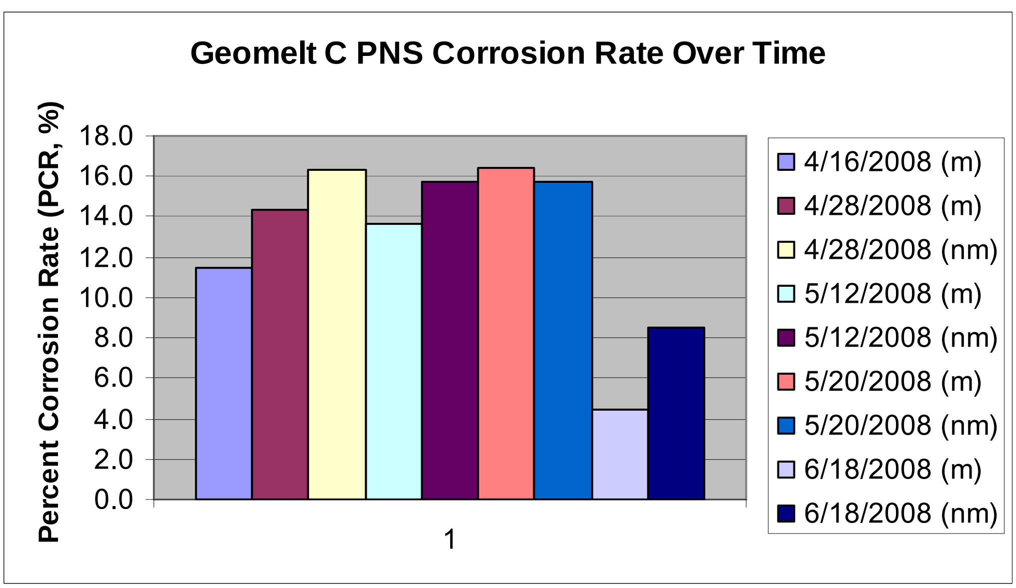


Figure 2.6 PNS/NACE cyclic emersion corrosion test results for Geomelt C, where ***m*** represents samples mixed in the field and ***nm*** represents samples not mixed.



Electrochemical Measurements

Electrochemical techniques to determine deicer corrosivity to metals provide an alternative to the gravimetric method in terms of allowing for the rapid determination of corrosion rate of metals and revealing information pertinent to the corrosion mechanism and kinetics.

The electrochemical technique was able to rapidly (within hours) evaluate the corrosivity of deicer products with or without corrosion inhibitors. Liquid samples collected to date have been tested with mild steel coupons (ASTM A36) using the electrochemical techniques. Table 2.1 shows some of the electrochemical data collected.

Table 2.1 Electrochemical data collected for deicers samples.

Freezeguard CI Plus		Corrosion Rate (MPY)	Impedence (Kohm cm^2)	Ecorr (mV, SCE)	Icor (μA/cm^2)
5/12/2008	mixed	22.6	0.36	-866.8	49.4
5/12/2008	not mixed	31.5	0.32	-878.6	69
6/18/2008	mixed	77.6	0.15	-870.4	169.8
6/18/2008	not mixed	36.0	0.30	-864.5	78.7
7/17/2008	mixed	42.5	0.27	-871.8	92.9

Geomelt C		Corrosion Rate (MPY)	Impedence (Kohm cm^2)	Ecorr (mV, SCE)	Icor (μA/cm^2)
5/12/2008	mixed	51.0	0.16	-764.2	111.7
5/12/2008	not mixed	56.5	0.17	-810.2	123.7
5/20/2008	mixed	44.0	0.20	-739.6	96.4
5/20/2008	not mixed	80.1	0.10	-748.3	175.4
6/18/2008	mixed	51.9	0.13	-712.0	113.6
6/18/2008	not mixed	13.8	1.10	-901.7	30.1
7/17/2008	mixed	26.7	0.30	-763.3	58.4
7/17/2008	not mixed	24.6	0.33	-762.4	54.3

NaCl+GLT		Corrosion Rate (MPY)	Impedence (Kohm cm^2)	Ecorr (mV, SCE)	Icor (μA/cm^2)
5/12/2008	mixed	13.5	1.10	-814.1	29.6
5/12/2008	not mixed	132.4	0.17	-844.9	289.8
5/20/2008	mixed	24.9	0.64	-825.5	54.4
5/28/2008	not mixed	47.2	0.53	-941.4	103.4
6/4/2008	mixed	64.5	0.38	-821.1	141.2
7/17/2008	mixed	43.2	0.49	-854.5	94.5
7/17/2008	not mixed	45.0	0.49	-910.0	98.4

The preliminary corrosion data of mild steel shows a weak correlation between the electrochemical data (E_{corr} and i_{corr}) and the PCR data collected using the PNS/NACE corrosion test. However, more data points are needed before we can make a definite conclusion. The original goal of this test was to establish a standard curve to correlate their corrosivity in PCR as a function of E_{corr} and i_{corr} for each deicer product. Then, for each type of deicer, a second standard curve will be established to correlate its E_{corr} and i_{corr} as a function of chloride and inhibitor concentrations. If such strong correlations do not exist, the electrochemical test can still be used as a QA/AC tool to detect any contamination or quality issues of the deicer product.

Task 2.3.: Method to Rapidly Quantify Deicer Performance (90%)

DSC Measurements

This task involves establishing a method to rapidly quantify deicer performance using a differential scanning calorimetry (DSC) thermogram instead of eutectic curve. DSC is an experimental technique that measures the energy necessary to maintain a near-zero temperature difference between the test substance and an inert reference material, with the two subjected to an identical (heating, cooling or constant) temperature program. By measuring the heat flow, DSC can detect phase transitions and quantify energy change, and measure kinetics of the transitions. DSC measurements typically require only a few milligrams of the sample, which is sealed in an aluminum capsule.

The eutectic temperature of a deicer is the temperature at which crystallization completes and the product becomes solid. A deicer featuring lower eutectic temperature does not necessarily have lower effective temperature or higher ice melting capacity. Therefore, we argue that the DSC thermogram provides a much better indication of the deicer performance than the widely-used eutectic curve (eutectic temperature as a function of deicer concentration). In fact, based on the DSC thermograms of a deicer at different concentrations, one can generate a more useful curve of effective temperature vs. deicer concentration, or even predicted ice melting capacity vs. deicer concentration.

Overall, the DSC thermogram provides useful information in regard to the thermodynamics of the deicer solution, which will provide insight into its freezing/thawing behavior in the absence of pavement. For instance, the characteristic temperature shown in Table 2.2 is a much more reliable indicator of the starting point of ice crystal growth than the eutectic temperature, which should correspond to the formation of slippery condition on pavement, or the "effective temperature" of the deicer applied.

Table 2.2 DSC data collected for deicer samples being monitored under storage

			Characteristic Temperature			Heat Flow (J/g)	
Sample		Date Collected	Average (°C)	Stdev	Average (°F)	Average	Stdev
Freezeguard Cl Plus	mixed	4/16/2008	-13.6	0.6	7.5	80.8	17.4
Freezeguard Cl Plus	mixed	4/28/2008	-11.9	0.2	10.6	104.7	10.9
Freezeguard Cl Plus	not mixed	4/28/2008	-12.3	0.3	9.9	102.9	19.3
Freezeguard Cl Plus	mixed	5/12/2008	-11.5	0.6	11.3	82.5	9.6
Freezeguard Cl Plus	not mixed	5/12/2008	-11.8	1.4	10.8	97.2	19.0
NaCl+GLT	mixed	5/12/2008	-21.8	0.1	-7.2	35.8	0.7
NaCl+GLT	not mixed	5/12/2008	-22.0	0.1	-7.6	20.9	14.2
NaCl+GLT	mixed	5/28/2008	-21.5	0.3	-6.7	44.1	1.4
Geomelt C	mixed	4/16/2008	-12.1	0.1	10.2	110.7	12.5

From recent efforts in another WTI project, we found a very reasonable correlation between heat flow (from DSC output, as shown in Table 2.2) and ice melting capacity (from SHRP tests at 32°F (0°C) after 60 minutes). The following preliminary results have been detailed in: [Fay, L., Shi, X.*, Volkening, K., Peterson, M.M. Laboratory Evaluation of Alternative Deicers: The Path to Decision-Making Based on Science and Agency Priorities. *Proceedings of the 88th Annual Meeting of Transportation Research Board*, Washington D.C., 2009, Paper number 09-2817. Also considered for publication in Transportation Research Record with revisions].

> The change in heat flow (ΔH) was calculated by subtracting the total heat of fusion for pure water (334 J/g) from the measured heat flow of the characteristic peak. Statistical analysis revealed the following correlation between the DSC data and the SHRP data at 0°C (32°F), as shown in Equation 1:
>
> $$\text{Ice Melting Capacity} = 0.66\times T + 8.58\times \text{Log}_{10}(\Delta H) - 4.86 \ (R^2=0.91) \qquad \text{Eqn. 1}$$
>
> The positive coefficient associate with $\text{Log}_{10}(\Delta H)$, i.e., 8.58, is consistent with the notion that the more powerful a deicer is, the less external heat it needs to melt the ice (and thus the higher value in ΔH). The high *R*-square value confirms that there is a strong correlation between the DSC data and the SHRP ice melting capacity

at 32°F (0°C). The less-than-one *R*-square can be attributed to: experimental error especially in the SHRP test, the different behavior between solid and liquid deicers in the SHRP test, etc. As such, DSC may hold the promise of a reliable standard test protocol to assess the deicer performance under certain road weather conditions.

Figures 2.7 and 2.8 are DSC thermograms for the liquid deicers and for Freezeguard CI Plus over time, respectively. For each type of deicer, their DSC thermogram was tested at a 2°C/min heating/cooling rate for inhibited solutions and the associated reagent grade product in order to determine if inhibitors contribute to freezing point suppression and if they provide any increase in the effectiveness of the deicers.

Figure 2.7 DSC thermograms of the three liquid products selected for this project.

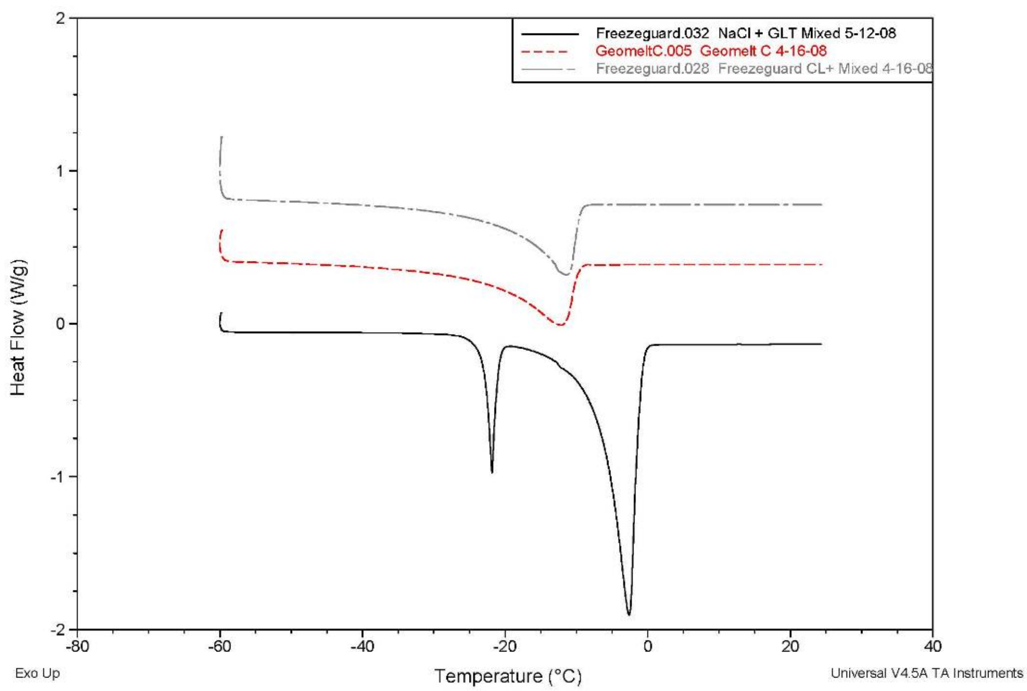
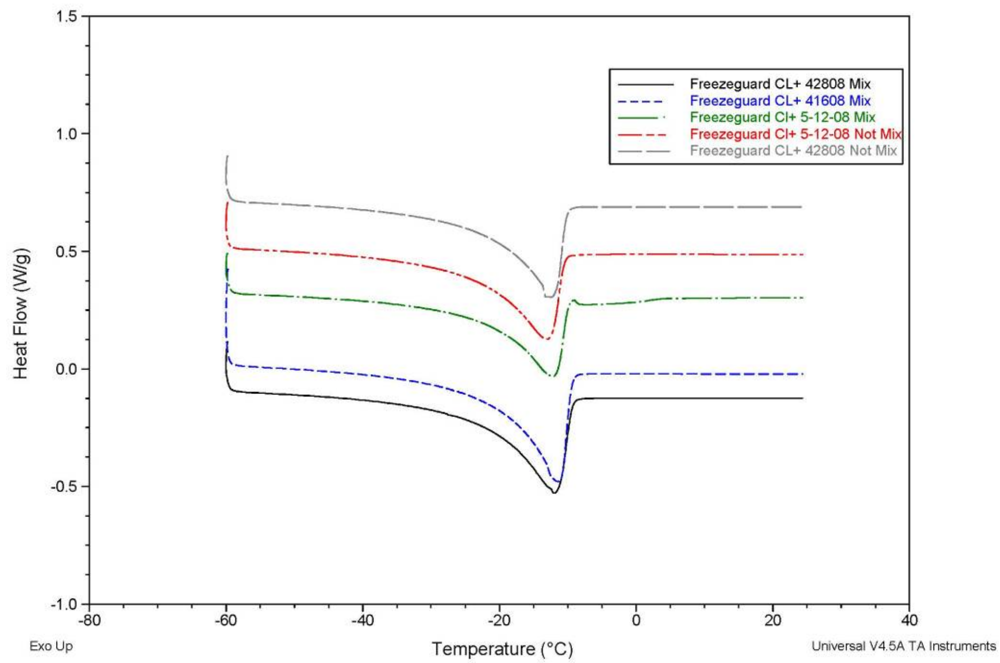


Figure 2.8 DSC thermograms of Freezeguard CI Plus over time.



Task 2.4.: Inhibitory Longevity under Laboratory Conditions (4%)

The material to make asphalt blocks was delivered to WTI by the Montana Department of Transportation and will be used to make asphalt blocks for testing the application methods, application rates and product recovery in the MSU sub-zero facility. The MSU sub-zero facility will become available in October 2008 at which time we anticipate testing to begin.

Task 3: Field Investigation (20%)

Task 3.1.: Inhibitor Longevity: Storage Monitoring

The UV-vis standard curves are being developed for the liquid deicers which will eventually allow us to quickly determine the corrosion inhibitor concentration over time.

Figures 3.1, 3.2, and 3.3 show the chloride concentrations of the liquid deicers over time, with a similar trend present in all where the not-mixed samples tend to have higher chloride concentrations than the mixed samples. This is most likely due to settling within the holding tanks and has been captured because all samples were collected from the bottom of the tanks. To further investigate this phenomenon we will sample each tank at varying depths over time. Please note that the chloride concentration of each deicer sample was not based on one single measurement of the as-received deicer sample, but rather based on chloride sensor measurement of multiple diluted samples and subsequent extrapolation (which minimizes the measuring error in the data).

Figure 3.1 Chloride concentrations of Geomelt C over time from mixed and not-mixed tanks.

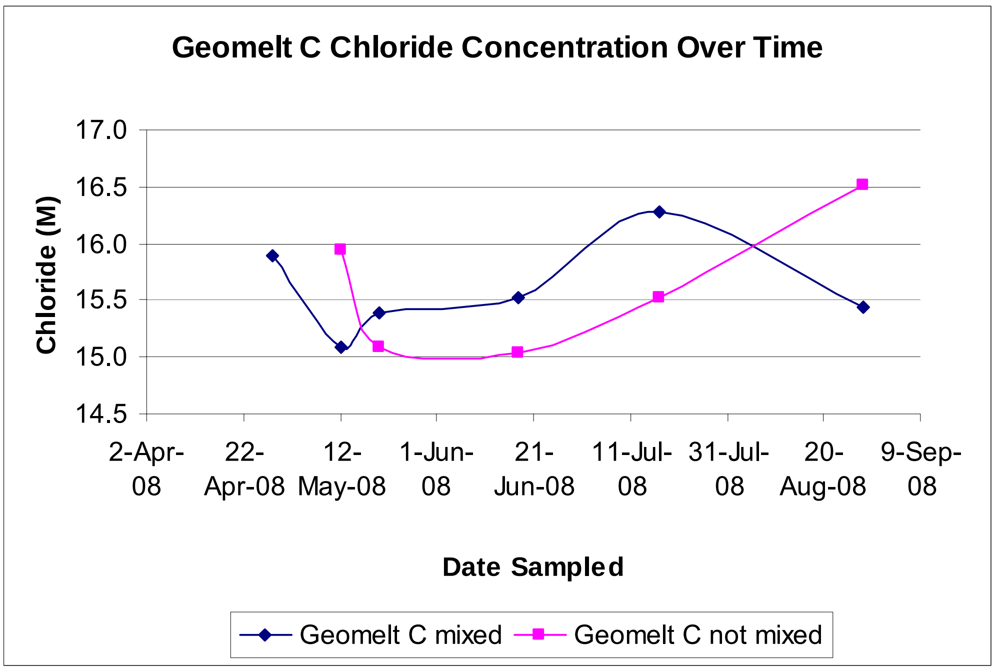


Figure 3.2 Chloride concentrations of Freezeguard CI Plus over time from mixed and not mixed tanks.

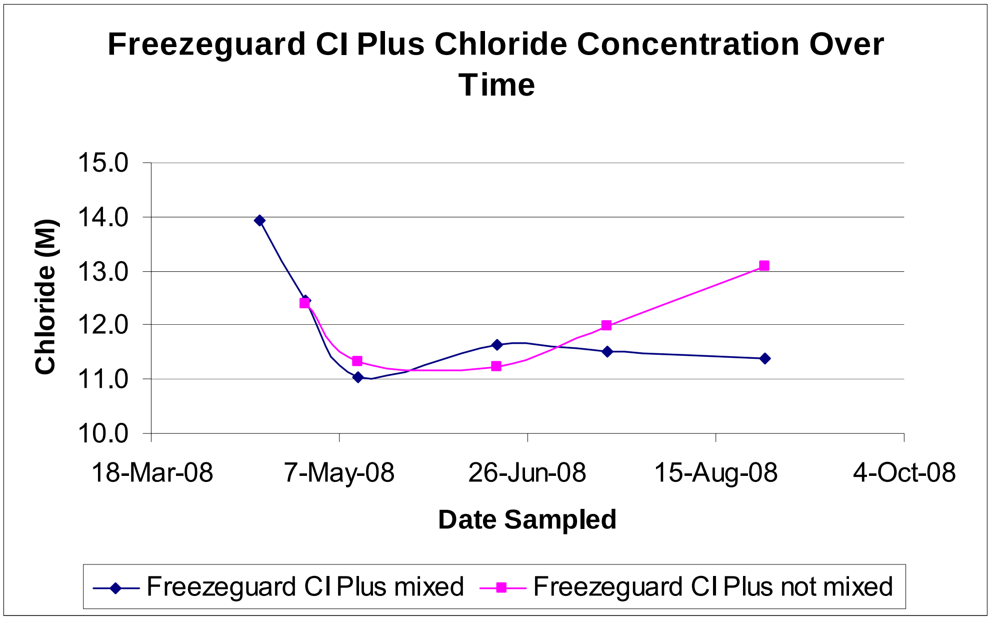
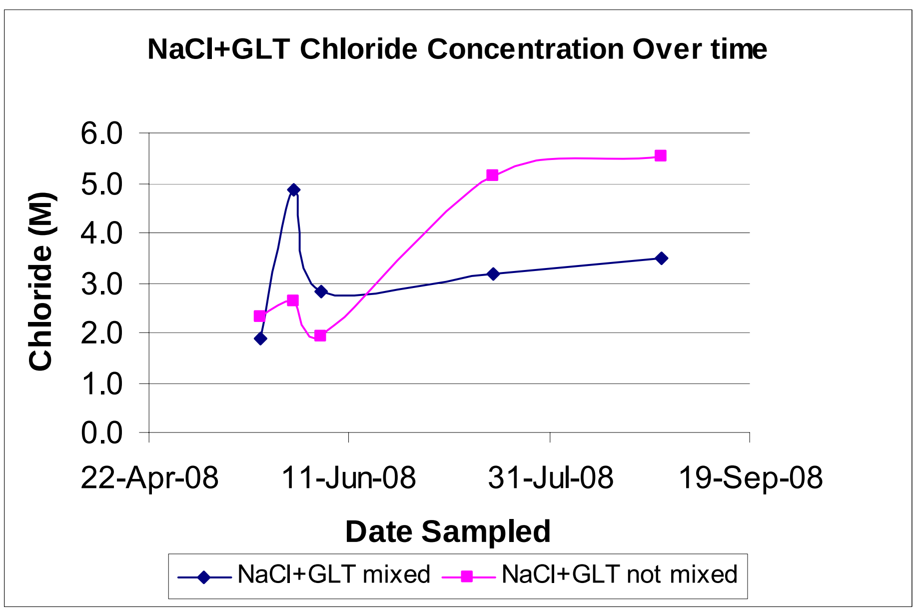


Figure 3.3 Chloride concentrations of NaCl+GLT (5%) over time from mixed and not mixed tanks.



The infrastructure outlined in the proposal has been completed. The second building was completed in September 2008 and will house the selected category 4 product.

Figure 3.4 Arial view of the *Transcend* field test site.

Task 3.2.: Inhibitor Longevity and Deicer Performance: Field Operational Tests

In the 2008-2009 winter season, the field operational tests will be conducted on a 200 x 600 ft pad of 2-inch asphalt overlay at *Transcend*. The products will be applied on the 600 ft length with sufficient spacing in the 200 ft width to prevent mixing. The four Turbo Crystal snow guns will be used to create the specified storms over this area. More details are being planned in the format of SOPs as described earlier.

Task 4: Project Reporting

This is the third project quarterly progress report. The next progress report will provide information through December 2008 and will be submitted January 2009.

Summary of Expenditures

Table 4.1 below summarizes the expenditures on this project through September 30, 2008. $213,468.21 has been spent by September 30, 2008, leaving $7,990.86 to be applied to the next project fiscal year. One solid inhibited product (PNS category 4) still needs to be obtained or purchased.

Table 4.1 Summary of Expenditures by September 30, 2008 (The Pooled Fund budget for 1/28/08-9/28/08 was $159, 126 and the rest was funded by the WTI-UTC).

Budget Category	Budget	Spent	Remaining
Labor ($)	$59,509.87	$58,310.33	$1,199.54
Travel	$2,000.00	$5,075.05	-$3,075.05
Operations/Communications	$400.00	$109.70	$290.30
Infrastructure start-up cost	$80,000.00	$79,922.66	$77.34
Contracted Testing Services	$3,500.00	$2,904.50	$595.50
Lewistown Facility Usage	$3,000.00	$0.00	$3,000.00
Corrosion Lab Testing and Other Supplies	$7,000.00	$3,480.01	$3,519.99
Total Direct Cost	$155,409.87	$149,802.25	$5,607.62
Indirect (42.5%)	$66,049.19	$63,665.96	$2,383.24
Total Cost ($)	$221,459.06	$213,468.21	$7,990.86

Project Schedule Summary

Table 4.2 details the updated project timeline, in which the duration of each task is shown by months.

Table 4.2: Project Timeline by Month

		Calendar Year / Month																																			
		2007			2008												2009												2010								
Tasks	***Milestones***	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9
Task 0. Project Management																																					
Project kickoff*	*Oct-07*																																				
Task 1. Experiment Design and Planning																																					
Task 2. Laboratory Investigation																																					
Task 2.1. Methods to Rapidly Quantify Chloride and Inhibitor Concentrations																																					
Task 2.2. Method to Rapidly Quantify Corrosivity of Deicers																																					
Task 2.3. Method to Rapidly Quantify Deicer Performance																																					
Task 2.4. Inhibitor Longevity under Laboratory Conditions																																					
Task 3. Field Investigation																																					
Task 3.1. Inhibitor Longevity: Storage Monitoring and Cost-Benefit Analysis																																					
Task 3.2. Deicer Performance: Field Application																																					
Task 4. Project Reporting																																					
Quarterly progress reports	*End of each quarter*																																				
Draft final report	*Jul-10*																																				
Final report w/ executive summary	*Sep-10*																																				

*UTC portion started 8/1/07 and the PNS portion start in Feb. 2008.

Appendix A. Meeting Notes for the Steering Committee Site Visit

The Steering Committee for the Pooled Fund Research into Inhibitor Longevity recently toured the lab facilities at Bozeman and the field study facility at Lewistown, now known as Transcend. Present for this tour were Ron Wright, Justun Juelfs, TAC Liaison Dan Williams, TAC member and Redmond Mineral rep Dave Wilkening, WTI researchers Laura Fay and Doug Cross, and Monty Mills. The Steering Committee wished to determine progress on the research thus far, as well as the facility build-up at Lewistown. While together, we had the opportunity to discuss many ongoing concerns regarding the goals and methodology of the research. The notes are divided the tour visits and discussions into 5 sections, as follows:

Lewistown/Transcend Facility

The facilities at Lewistown are largely in place. The six 3000 gallon tanks have product, and the agitated tanks are activated on a regular basis by the research assistants. Two covered buildings are in place, and the pads for the uncovered stockpiles are also built. At this time, only one building and one pad have product - a salt sand mix. The other two facilities are awaiting a Category 4 product.

While we were there, a well was being drilled and had hit water at the 600 foot depth. It is expected that this would provide sufficient water to run the snowmaking machinery for the field trials. That machinery is on order and expected to be up and running this winter for the first round of field trials. Electricity is also being pursued for the facility to eliminate reliance on generators. The weather station and lighting is currently running on solar power.

While at Lewistown, we discussed some additional concerns about material collection in the cisterns which WTI will address. They will also build a smaller solid storage control pad to more accurately assess precipitation and evaporation rates to apply to the larger pads. Other items discussed were a snow fence to prevent drifting into the control area, and tarp-covers for the entrances to the covered storage to prevent snow and rain encroachment.

Field Testing

The discussion about how to collect viable samples from the pavement is still occurring. Obviously the timeline for this is very tight and WTI plans to focus their effort on getting the best method identified and tested.

Also discussed was the method by which liquid product is applied - stream or spray. WTI will test both methods in the lab to determine percent recovery. Both methods may be used in the research - one for collection (spray) and the other for performance (stream).

Grid lines need to be established on the asphalt as reference for field collection.

Field testing is expected to begin this January with two artificial events and one natural event. More to come on this.

Lab

All of the critical lab equipment is now in place, including the Corrosion Testing Machine and the DSC. This equipment is up and running and being used to test the research materials and establish ways to test for inhibitor presence and concentration. The materials to produce the asphalt slabs have been provided by MDT and delivered to WTI. WTI will produce the asphalt slabs in order to begin laboratory testing on the percent recovery of deicers applied on pavement.

Weather Events

1) Black Ice Event - freezing fog/drizzle with 1/10 to 1/500 inch of precip on pavement. Air temp - 25 to 32 degrees F. Pavement temp lower than ambient air temp.

2) Snow Event - 2 to 4 inches snow. Air temp - 25 to 32 degrees F. Pavement temp 25 to 32 degrees F. Little or no wind to prevent drifting snow onto test plot.

3) Natural Event.